in Greece. He is now engaged in preparing a comprehensive memoir on the subject which may be expected to throw new light on some questions of historical geography.

MR. MACKINDER, in his fifth lecture for the Royal Geographical Society's education scheme, spoke of the chief lines of communication between Asia and Europe and the ways by which successive bands or hordes of Asiatic invaders forced a passage into the heart of Europe. The routes across Asia Minor from the Gate of Cilicia to the northern waters, and the thoroughfare through the Balkan peninsula now traversed by the international railway, were shown to have guided the movements of peoples and the formation or dissolution of nations from the dawn of European history on to the present day.

THE United States appears to have entered the field as an aggrandising power, taking up territory beyond the limits of the continent of North America. The annexation of Hawaii seems likely to be effected without remonstrance, and a footing has also been obtained in San Domingo, the eastern part of the island of Haiti.

MR. A. VAUGHAN WILLIAMS has been exploring the region round the mouth of the Sabi River in south-east Africa. He has ascended the stream for thirty miles to the limit of tidal influence.

THE orthography of African place names is a perpetual source of confusion. It appears that in place of Zimbabwe or Zimbabye we ought, in order to render the sound of the word used by the people surrounding the ruins, to write "Zimbabghi." The familiar name Mashonaland is in itself a corruption of the native name, but is always pronounced Mashunaland, a pronunciation to which the spelling ought to conform.

RAILWAYS seem likely at last to become established in China. The line from Teintsin to Taku has now been extended to the River Lan, a total distance of 130 miles, and is being rapidly pushed northward, a considerable section being already opened for passenger traffic.

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## CAPTAIN BOWER'S JOURNEY IN TIBET.

AT an extra meeting of the Royal Geographical Society, on Monday night, Captain H. Bower described his recent journey with Dr. Thorold across Tibet from west to east. They set out from Leh on June 14, 1891, and were fortunate enough to get well into Tibet before meeting any natives. Travelling due east they crossed a pass of 18,400 feet, on the other side of which lay the Horpa Cho, the highest lake yet met with in Tibet, and probably the highest in the world, its altitude being 17,930 feet. Along the route eastward many other lakes were passed, all salt and without outlet, the want of fresh water being sometimes severely felt; a kettleful of hailstones was a welcome catch on one occasion. The travellers used ponies and donkeys for carrying their loads, as yaks do not eat grain, and grass was often not met with for many days' journey. At length, after travelling east and south-east for about 700 miles, they were stopped within 200 miles of Lhasa by the Tibetans, who paid no attention to Chinese passports, and after much parleying insisted on a complete change of route. The party had to retrace their steps for several days' march, turn northward, and then make their way east at a safer distance from the capital. It was now the month of October and the crossing of passes over 18,000 feet, with temperatures of 15° or more below zero, in strong wind was extremely trying. About the end of November, for the first time for four months, the tents were pitched at a less altitude than 15,000 feet, and soon afterwards Chiamdo was reached. Here great difficulty was experienced with the lamas, who insisted that no European should enter the town; but by the intervention of the Chinese Amban, whose power was really but slight, the party was allowed to proceed, passing round the outside of the town. From Chiamdo to Batang the way was easy, and no difficulties were experienced thereafter. At Ta-Chen-Lu they entered China and reached Shanghai on March 29, 1892. Throughout Central Tibet the authorities disclaimed the sovereignty of China, maintaining that only the grand lama had jurisdiction in that region. Many of the lamas met with were educated and intelligent men, but not inclined to give information. Much difficulty was experienced in getting the names of lakes and mountains, no two Tibetans giving the same answer. The fanaticism and distrust of the people created constant difficulties, but Captain Bower, under the pretext of being a Buddhist with a peculiar ritual, succeeded in making observations for position openly as part of a religious service, previous attempts to do so by stealth having failed.

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## THE CHEMISTRY OF OSMIUM.

AN important addition to our knowledge of the chemical nature of this interesting element is contributed by Prof. Moraht and Dr. Wischin, of Munich, to the current number of the *Zeitschrift für Anorganische Chemie*. Two years have scarcely elapsed since the position of osmium in the periodic system was finally decided by the painstaking re-determination of its atomic weight by Prof. Seubert. Previous determinations of the atomic weight of osmium had been made with material which Seubert subsequently showed to be impure, and in consequence the erroneous value, 198·6, had been ascribed to it. Indeed previous to the year 1878 the order of precedence as regards atomic weight of the four metals of the platinum group --gold 196·2, iridium 196·7, platinum 196·7, and osmium 198·6 —was entirely at variance with the order demanded by their chemical and physical properties, and a standing contradiction of the periodic law of Newlands and Mendeleef. In that year, however, Seubert attacked the case of iridium, and as the result of a series of determinations, made with the laborious care which has characterised all his work, the atomic weight of this metal, when obtained in a pure state, was shown to be 192·5, a number very different to that previously assigned to it, and which was afterwards remarkably confirmed, even to the decimal place, by an independent investigation by Joly. Three years later Seubert made his celebrated re-determination of the atomic weight of platinum, which resulted in the number 194·3 being finally derived for the true atomic weight of the perfectly pure metal. This value was likewise subsequently confirmed by Halberstadt. In the year 1887 the position of gold was decided by simultaneous independent re-determinations of its atomic weight by Thorpe and Laurie in this country and Krüss in Germany, the two values being practically identical, 196·7. Lastly, in 1891, Seubert completed his work by re-determining the atomic weight of osmium with a specimen of the metal of practically perfect purity, with the result that the old number, 198·6, was found to be entirely erroneous, due to considerable quantities of impurities being present in the samples previously employed, and that the real value of this constant was 190·3, thus removing osmium from its former situation at the end of the series and placing it in its proper position at the head of it.

The order of precedence of the metals of the platinum group is therefore as follows:—Osmium 190·3, iridium 192·5, platinum 194·3, and gold 196·7. This order is in full accordance with the relative chemical and physical properties of these metals, and the last outstanding exception to the periodic generalisation has disappeared.

Although the properties of pure metallic osmium, and particularly its atomic weight, are now known with certainty, the nature of its compounds is yet very little understood. Moreover, it is evident from the result of the investigation of Prof. Seubert that previous workers have been dealing with an impure metal of atomic weight, 198·6. It was therefore desirable that not only should the chemistry of this element be extended to compounds hitherto uninvestigated, but that the composition and properties of the compounds already known should be subjected to a re-examination.

Prof. Moraht and Dr. Wischin have therefore taken up the study of the compounds of osmium with oxygen, sulphur, and the halogens, employing material of a very high degree of purity, and the results of their investigation are both novel and interesting.

Work with osmium compounds is endowed with peculiar personal danger to the chemist, owing to the great facility exhibited under the most various conditions for the formation of the tetroxide $OsO_4$, a substance which boils at 100° C., and is very volatile at the ordinary temperature, and which attacks the skin, the lungs, and particularly the eyes with most serious consequences.

The material started with was a comparatively pure sample of the best known salt containing osmium, potassium osmate, $K_2OsO_4.2H_2O$. This salt was further purified by distillation with nitric acid or aqua regia and absorption of the liberated tetroxide vapours in a solution of caustic potash. The dark brown solution of potassium perosmate thus formed was largely diluted with water, and reduced to osmate by the addition of alcohol. After the expiration of about twenty-four hours almost the whole of the osmium had separated in the form of beautiful little crimson octahedrons of the salt $K_2OsO_4.2H_2O$, which, after washing with dilute alcohol, proved to be quite free from impurity, showing no trace of iridium.

Previous observers have noticed that an aqueous solution of *potassium osmate*, $K_2OsO_4$, is most remarkably affected by sunlight, a rapid decomposition being brought about with deposition of a black precipitate to which the composition $OsO_2.2H_2O$ has been ascribed. The specimens experimented with, however, undoubtedly contained iridium, and it was therefore of interest to investigate the action of sunlight upon solutions of the pure salt just described. When the crimson octahedrons of pure $K_2OsO_4.2H_2O$ were dissolved in cold water, and the clear reddish violet-coloured solution was exposed to direct sunshine, no evidence of change was apparent for several days, but the moment the vessel containing the solution was immersed in a bath of boiling water, while in bright sunshine, decomposition commenced, and a black precipitate rapidly accumulated, until after the expiration of two or three hours the whole of the osmium present was deposited. As there is a marked tendency for the production of the noxious fumes of osmium tetroxide during this decomposition of the hot osmate solution by the waves of light it is best to take the precaution of reducing their amount to a minimum by the addition of a little alcohol, which acts as a strong reducing agent under these circumstances, and by passing a stream of hydrogen through the solution during the whole operation. The precipitate is usually so finely divided that considerable difficulty is experienced in separating it from the solution. The filtration succeeds best when the filter is previously moistened with dilute acetic acid, when a clear colourless filtrate is usually at once obtained. The precipitate cannot be dried in a warm air bath, as it is largely converted thereby into the volatile osmium tetroxide. It may safely, however, be dried over phosphoric anhydride in the vacuum of an air-pump.

The accurate analysis of an insoluble substance of the nature of this precipitate, and containing a metal such as osmium, which so readily oxidises to the volatile tetroxide, is a task of exceptional difficulty. The usual method of reduction to metal in a stream of hydrogen is insufficient, for more or less of the tetroxide is always formed during the process, necessitating the use of an absorption apparatus containing a solution of caustic potash, placed in front of the tube containing calcium chloride to absorb the water formed. The difficulty is, then, how to estimate the small quantity of osmium thus dissolved in the large excess of alkali. It was eventually found that the weak electric current from three Daniell's cells precipitates the whole of the osmium from such a solution, contained in a nickel dish which forms the negative electrode, in the form of pure *osmium dioxide*, $OsO_2$, which may conveniently be dried *in vacuo* over phosphoric anhydride and weighed as such.

By this mode of analysis the interesting fact was eventually elicited, that the black insoluble substance formed by the action of light upon a hot solution of potassium osmate is not, as was previously supposed, a hydrate of osmium dioxide of the composition $OsO_2.2H_2O$, but is no other than free *osmic acid* itself, the hydrate of osmium trioxide, $OsO_3.H_2O$ or $H_2OsO_4$. Osmic acid is thus formed by the direct action of water, under the influence of sunlight and slight rise of temperature, upon the potassium salt. This remarkable change is expressed by the simple equation:

$$K_2OsO_4 + 2H_2O = H_2OsO_4 + 2KOH.$$

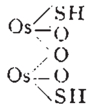
The liquid, as soon as the change commences, is observed to exhibit a strong alkaline reaction, becoming, as indicated in the equation, a solution of caustic potash. It is singular that the presence of alcohol and the passage of a current of hydrogen during the reaction do not cause any reduction, serving only to hinder the further oxidation to the state of tetroxide. Indeed, if the crimson octahedral crystals of potassium osmate are covered in sunshine with warm alcohol and a current of hydrogen is allowed to bubble through the liquid, no trace of blackening is observed upon the faces of the crystals. The moment water is added, however, decomposition is immediately brought about.

*Osmic acid*, $H_2OsO_4$, is a soot-black powder, which fumes strongly in moist air, owing to its rapid conversion into the volatile osmium tetroxide, $OsO_4$, but which is quite permanent at the ordinary temperature when preserved under water containing alcohol. It dissolves readily in nitric acid with formation of the hydrate of osmium tetroxide, the so-called per-osmic acid. Cold hydrochloric acid attacks it but very slightly. Upon warming, however, it is entirely soluble, forming an olive-green liquid, which will be subsequently considered, with liberation of a small quantity of chlorine. Sulphuric acid does not attack it. Osmic acid reacts in a most energetic and interesting manner with sulphuretted hydrogen gas. Even in the dry state at the ordinary temperature the reaction proceeds with considerable violence. If the experiment is conducted in a piece of combustion tubing, upon which a bulb has been blown for the reception of the osmic acid, the moment that the gas enters the tube the whole of the black powder immediately becomes incandescent, and drops of water and a large quantity of free sulphur are deposited in the portion of the tube not heated by the reacting substances. The residual product of the reaction is a brown powder, which has been found to be a hydrated oxysulphide of osmium of the composition $2OsSO.H_2O$.

The reaction occurs in accordance with the equation—

$$2H_2OsO_4 + 4H_2S = 2OsSO.H_2O + 5H_2O + 2S.$$

This *oxysulphide of osmium* is soluble in acids with decomposition, even sulphuric acid decomposing it with evolution of sulphuretted hydrogen. It possesses acid properties, for it liberates carbon dioxide from carbonate of soda and sulphuretted hydrogen when fused with sulphide of potassium. It would, moreover, appear to contain SH groups, for it yields mercaptan upon treatment with soda and ethyl iodide, the osmium being reduced to the dioxide $OsO_2$. Its probable constitution is therefore represented by the graphic formula:—



When this oxysulphide is warmed in dry sulphuretted hydrogen another violent reaction occurs, the whole mass again becomes incandescent, and the whole of the oxygen is eliminated in the form of water. The product of this second reaction with sulphuretted hydrogen is pure *osmium disulphide* $OsS_2$.

$$Os_2O_3(SH)_2 + 2H_2S = 2OsS_2 + 3H_2O.$$

Of the *halogen* compounds of osmium only the chlorides have been at all investigated, chiefly by Claus, whose observations may be summarised in a few words.

When finely-powdered metallic osmium is heated in a stream of dry chlorine sublimates are formed. The first chlorine compound formed is chromous-green in colour, but is only produced to a very slight extent. There is next deposited a dense black sublimate, and finally a smaller quantity of a sublimate of the colour of red lead. None of these three chlorine compounds are crystalline. Claus subsequently stated that the lowest chloride OsCl, is a bluish-black solid when isolated, and forms a dark bluish-violet solution; the sesquichloride $Os_2Cl_3$ is reddish-brown in the solid state, and gives with water a rose-red coloured solution, and the dichloride $OsCl_2$ is the compound which exhibits the colour of red-lead, and yields a lemon-yellow solution

These observations of Claus are completely confirmed by the experiments of Prof. Moraht and Dr. Wischin, who, however, have extended them, and have been able to isolate other and higher chlorides of osmium.

They commenced by warming a large quantity of the free osmic acid above described for two days upon a water-bath with concentrated hydrochloric acid, the flask in which the reaction was conducted being connected with an upright condenser. A little alcohol was added in order to prevent the formation of osmium tetroxide. The osmic acid eventually entirely dissolved with formation of the dark olive-green coloured solution previously incidentally mentioned, a little chlorine being evolved at the commencement of the operation. It was found impossible to evaporate the solution upon the water-bath without decomposition, but evaporation *in vacuo* over sulphuric acid and solid caustic potash, the latter to absorb the hydrochloric acid, succeeded admirably. The solid left after complete evaporation consisted of well formed crystals which assumed the habit of six-sided pyramids. These crystals were dark olive-green in colour when moist, but when the last traces of superfluous water were removed, exhibited a bright vermilion colour. They were readily soluble in water and alcohol, the solutions being coloured dark green, and the salt may be recrystallised from these solvents. Upon analysis they were found to consist of the chloride $Os_2Cl_7$ crystallised with seven molecules of water.

This chloride of osmium, $Os_2Cl_7.7H_2O$, would appear to be a molecular compound of the *trichloride*, $OsCl_3$, and the *tetrachloride*, $OsCl_4$. For when potassium chloride solution is added to the solution of the crystals in alcohol, a precipitate of brilliant red octahedrons and cubes of potassium osmichloride, $K_2OsCl_6$, is obtained, showing the presence of *osmium tetrachloride*, $OsCl_4$. Moreover, when the precipitate is separated by filtration, and the filtrate concentrated by evaporation *in vacuo*, dark green crystals of the *trichloride*, $OsCl_3$, are deposited containing three molecules of water of crystallisation.

During the reduction of these crystals of the trichloride in a current of hydrogen for the purposes of analysis, a small quantity of a white sublimate was obtained, which probably consisted of the *octo-chloride*, $OsCl_8$, corresponding to the tetroxide $OsO_4$.

Bromine does not react with osmium with anything like the energy of chlorine. The free elements do not appear to combine at all, even at moderately high temperatures. Only a small quantity of a sublimate of a dark brown colour is obtained by passing bromine vapour over osmic acid. This sublimate dissolves to a brown solution in water, which, however, rapidly decomposes with deposition of a black precipitate.

When osmic acid, $H_2OsO_4$, is treated with hydrobromic acid in the manner just described in the case of hydrochloric acid a similar reaction occurs with formation of a clear reddish-brown solution which yields, upon evaporation *in vacuo* over sulphuric acid and solid caustic potash, small crystals of a molecular compound of the *tribromide*, $OsBr_3$, and the *hexabromide*, $OsBr_6$, together with six molecules of water of crystallisation. These crystals of $Os_2Br_9.6H_2O$ are dark reddish-brown in colour and exhibit a beautiful metallic lustre. They are quite stable when preserved in a dry atmosphere, but rapidly deliquesce in moist air.

Iodine appears to possess even less affinity for osmium than bromine. When, however, osmic acid is treated with hydriodic acid a deep greenish-brown solution is obtained which deposits *in vacuo* dark violet rhombohedrons, exhibiting a brilliant metallic lustre, consisting of the anhydrous *tetra-iodide of osmium*, $OsI_4$. This iodide, the only one containing osmium yet prepared, is permanent in a dry atmosphere at the ordinary temperature, but rapidly deliquesces like the bromide when exposed to moist air.

In relative stability the chloride bromide and iodide of osmium above described exhibit a gradation such as would be expected from the relations between the halogen elements themselves. The iodide is readily dissociated by slightly raising the temperature, and upon the addition of water is decomposed with the deposition of a black precipitate containing the metal. A similar decomposition occurs, although much more slowly, in case of the bromide. The chloride, however, is well-nigh permanent under these conditions, only exhibiting traces of decomposition after the lapse of a considerable time. A. E. TUTTON.

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## REDUCTION OF TIDAL OBSERVATIONS.[1]

THE tidal oscillation of the ocean may be represented as the sum of a number of simple harmonic waves which go through their periods approximately once, twice, thrice, four times in a mean solar day. But these simple harmonic waves may be regarded as being rigorously diurnal, semi-diurnal, ter-diurnal, and so forth, if the length of the day referred to be adapted to suit the particular wave under consideration. The idea of a series of special scales of time is thus introduced, each time-scale being appropriate to a special tide. For example, the mean interval between successive culminations of the moon is 24h. 50m., and this interval may be described as the mean lunar day. Now there is a series of tides, bearing the initials $M_1$, $M_2$, $M_3$, $M_4$, &c., which go through their periods rigorously once, twice, thrice, four times, &c., in a mean lunar day. The solar tides, S, proceed according to mean solar time, but, besides mean lunar and mean solar times, there are other special time scales appropriate to the other tides.

The process of reduction consists of the determination of the mean height of the water at each of twenty-four special hours, and subsequent harmonic analysis. The means are taken over such periods of time that the influence of all the tides governed by other special times is eliminated.

The process by which the special hourly heights have hitherto been obtained is the entry of the heights observed at the mean solar hours in a schedule so arranged that each entry falls into a column appropriate to the nearest special hour. Schedules of this kind were prepared by Mr. Roberts for the Indian Government.[1] The successive rearrangements for each sort of special time were made by recopying the whole of the observations time after time into a series of appropriate schedules. The mere clerical labour of this work is enormous, and great care is required to avoid mistakes.

All this copying might be avoided if the observed heights were written on movable pieces. But a year of observation gives 8760 hourly heights, and the orderly sorting and resorting of nearly 9000 pieces of paper or tablets might prove more laborious and more treacherous than recopying the figures.

The marshalling of movable pieces might, however, be reduced to manageable limits if all the twenty-four observations pertaining to a single mean solar day were moved together, for the movable pieces would be at once reduced to 365, and each piece might be of a size convenient to handle.

The realization of this plan affords the subject of this paper, and it appears that not only is all desirable accuracy attainable, but that the other requisite of such a scheme is satisfied, namely, that the whole computing apparatus shall serve any number of times and for any number of places.

The first idea which naturally occurred was to have narrow sliding tablets which should be thrown into their places by a number of templates. It is unnecessary to recount all the trials and failures, but it will suffice to say that the slides and templates would require the precision of a mathematical instrument if they are to work satisfactorily, and that the manufacture would be so expensive as to make the price of the instrument prohibitive.

The idea of making the tablets or strips to slide into their places was accordingly abandoned, and the strips are made with short pins on their under sides, so that they can be stuck on to a drawing board in any desired position. The templates, which were also troublesome to make, are replaced by large sheets of paper with numbered marks on them to show how the strips are to be set. The guide sheet is laid on a drawing board, and the pins on the strips pierce the paper and fix them in their proper positions.

The strip belonging to each mean solar day is divided by black lines into 24 equal spaces, intended for the entry of the hourly heights of water. The strip is nine inches long by $\frac{1}{5}$ inch wide, and the divisions ($\frac{3}{8}$ by $\frac{1}{5}$) are of convenient size for the entries. There was much difficulty in discovering a good material, but after various trials artificial ivory, or xylonite, was found to serve the purpose. Xylonite is white, will take writing with Indian ink or pencil, and can easily be cleaned with a damp cloth. It is just as easy to write with liquid Indian ink as with ordinary ink, which must not be used, because it stains the surface.

The observations are to be treated in groups of two and a half lunations or 74 days. A set of strips, therefore, consists of 74, numbered from 0 to 73 in small figures on their flat ends.

If a set be pinned horizontally on a drawing board in vertical column, we have a form consisting of rows for each mean solar day, and columns for each hour. The observed heights of the water are then written on the strips.

When the twenty-four columns are summed and divided by the number of entries we obtain the mean solar hourly mean heights. The harmonic analysis of these means gives the mean solar tides. But for evaluating the other tides the strips must be rearranged, and to this point we turn our attention.

Let us consider a special case, that of mean lunar time. A mean lunar hour is about 1h. 2m. m.s. time; hence the 12h. of each m.s. day must lie within 31m. m.s. time of a mean lunar

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[1] "On an Apparatus for facilitating the Reduction of Tidal Observations." By G. H. Darwin, F.R.S., Plumian Professor and Fellow of Trinity College, Cambridge. A paper read before the Royal Society on December 15, 1892.

[1] An edition of these computation forms was reprinted by aid of a grant from the Royal Society, and is sold by the Cambridge Scientific Instrument Company, but only about a dozen copies now remain.